

Iodine-129, Iodine-127 and Caesium-137 in the environment: soils from Germany and Chile

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ABSTRACT

Soil profiles from Bavaria in southern Germany and from Chile were analysed for ¹²⁹I by accelerator mass spectrometry (AMS), for ¹²⁷I by inductively coupled plasma mass spectrometry (ICP-MS), and for ¹³⁷Cs by gamma-spectrometry. The mean deposition density of ¹³⁷Cs in soils from Bavaria was $(41 \times 1.5^{\pm 1}) \text{ kBq m}^{-2}$ (geometric mean and geometric standard deviation), originating mostly from the Chernobyl fall-out. The deposition density of ¹²⁹I in these soils was $(109 \times 1.5^{\pm 1}) \text{ mBq m}^{-2}$. The dominant sources of ¹²⁹I in Bavaria are, however, the reprocessing plants La Hague and Sellafield and not the Chernobyl fall-out. The ¹²⁹I/¹²⁷I isotopic ratios of the Bavarian soils were between 10^{-7} and 10^{-10} , i.e. 10^2 – 10^5 times higher than the ratios observed for the samples from Chile. The ¹²⁹I integral deposition densities in Chile, Easter Island and Antarctica were between 0.3 mBq m^{-2} and 2 mBq m^{-2} . In these soils, the observed ¹²⁹I/¹²⁷I ratios were about 10^{-12} . The soils from Chile allow the determination of the ¹²⁹I fall-out from the atmospheric nuclear weapons explosions undisturbed from contaminations due to releases from reprocessing plants. An upper limit of the integral ¹²⁹I deposition density of the atmospheric nuclear weapons explosions on the Southern Hemisphere (27°S) is about 1 mBq m^{-2} . Finally, the dependence of the migration behaviour of ¹³⁷Cs, ¹²⁷I and of ¹²⁹I on the soil properties is discussed. It turns out that there is a distinctly different behaviour of ¹²⁷I, ¹²⁹I, and ¹³⁷Cs in the soils exhibiting different sorption mechanisms for old and recent iodine as well as for ¹³⁷Cs.

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1. Introduction

The long-lived radionuclide ¹²⁹I ($t_{1/2} = 15.7 \text{ Ma}$) is naturally produced by cosmic-ray induced spallation of xenon in the atmosphere and by spontaneous fission of ²³⁸U. The total natural ¹²⁹I inventory of the geosphere was estimated by Fabryka-Martin (1982) to be 50,000 kg (326.8 TBq); see Schmidt et al. (1998) for details and further references. Most of this inventory is bound in the lithosphere and just 263 kg (1.7 TBq) is the “mobile” inventory of atmosphere, hydrosphere and biosphere. The main natural sources of mobile ¹²⁹I are releases from lithosphere through volcanic activity and production by cosmic radiation (about 45% each). In atmosphere, hydrosphere and biosphere, ¹²⁹I mixes with stable ¹²⁷I and enters the environmental iodine cycle. Over long time scales, equilibrium between ¹²⁹I and ¹²⁷I can be assumed in the mobile inventory.

The natural equilibrium of the ¹²⁹I/¹²⁷I isotopic ratios was estimated to be in the range of $(0.04\text{--}3.0) \times 10^{-12}$ (Edward, 1962; Edwards and Rey, 1968; Kohman and Edwards, 1966). Using a detailed equilibrium model Fabryka-Martin et al. (1984) calculated an isotopic ratio of 5.5×10^{-13} for the marine hydrosphere and for soils and the terrestrial biosphere a slightly higher ¹²⁹I/¹²⁷I isotopic ratio of 6.5×10^{-13} . Measurements of young oceanic sediments yielded a value of $^{129}\text{I}/^{127}\text{I} = \sim 1.5 \times 10^{-12}$ (Fehn et al., 1986; Schink et al., 1995; Moran et al., 1998). A pre-nuclear equilibrium ¹²⁹I/¹²⁷I isotopic ratio of $(2.0 \times 1.4^{\pm 1}) \times 10^{-13}$ in the continental biosphere was proposed on the basis of pre-nuclear iodine preparations (Ernst, 2003; Ernst et al., 2003).²

More than 99% of the mobile ¹²⁷I, about $8 \times 10^{14} \text{ kg}$, is contained in the oceans and young oceanic sediments (Fabryka-Martin et al., 1984). According to Muramatsu and Wedepohl (1998) most of the iodine in the Earth's crust is contained in marine sediments (68%) and only 0.8% is dissolved in the seawater. Igneous and metamorphic rocks contain only 2.7%, marine basalts 0.6% and

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² We use the convenient notation of $2.0 \times 1.4^{\pm 1}$ to present geometric means, here 2.0, and geometric standard deviations, here 1.4.

sedimentary rocks 28%. Most authors agree that the ^{127}I in the atmosphere and biosphere originates mainly from marine sources (Miyake and Tsungai, 1963; Kocher, 1981; Whitehead, 1984).

Iodine is released not only from the ocean surface mainly as CH_3I , but also as I_2 and HOI . A complex photochemistry oxidises the iodine species to I^- and IO_3^- . The atmospheric iodine makes its way to the continents where it is deposited by wet and dry deposition. The precipitation interacts with soils and the iodine is partially adsorbed in the soils. Surface and groundwater transport iodine back into the oceans. A complicated compartment system with highly differing time scales must be assumed to describe the pathways in the global mobile iodine inventory. Locally, the situation is even more complicated. On the way of the air masses over the continents, the atmospheric iodine is depleted resulting in lower deposition rates deep inside the continents compared to ocean-near areas. See Fabryka-Martin et al. (1984), Yoshida and Muramatsu (1995), Cox et al. (1999), Amachi et al. (2001), Muramatsu et al. (2004), Baker (2005), Pechtl et al. (2007), O'Dowd and Leeuw (2007), and Englund et al. (2010) for further details and discussions.

Iodine in surface water and soils are the essential sources of iodine in the terrestrial biosphere. Iodine is a biophilic element and enriched in organic materials such as proteins, polyphenols and humic substances. Large amounts of ^{127}I and ^{129}I in freshwater, estuaries and oceanic surface waters are associated with macro-molecular organic matter (Schall et al., 1997; Moore and Grosko, 1999; Schwehr and Santschi, 2003).

Man-made ^{129}I has been released into the environment by atmospheric atomic explosions, nuclear fuel reprocessing facilities and nuclear reactor accidents. Nuclear fuel reprocessing is the important source of the man-made ^{129}I into the environment. As discussed in detail elsewhere (Michel et al., 2012), estimates of the ^{129}I releases from atmospheric atomic explosions range from 43 kg (0.28 TBq) to 150 kg (0.98 TBq) and of the Chernobyl accident from 2 kg (13 GBq) to 6 kg (40 GBq). Up to the year 2005, the European reprocessing plants, La Hague and Sellafield discharged 251 kg (1.64 TBq) into the atmosphere and 4720 kg (30.9 TBq) into the English Channel and the Irish Sea, respectively. For the reprocessing plant Marcoule estimates of the atmospheric discharges are between 68 kg (0.45 TBq) and 184 kg (1.2 TBq). No estimates of the discharges into the Rhone River are available for Marcoule. For the other, in particular the military, reprocessing plant only few data exist, so that any estimate of the global releases remains incomplete.

Human nuclear activities and the associated releases of man-made isotopes are heavily concentrated in the Northern Hemisphere. Only three nuclear power plants and two reprocessing plants are located in the Southern Hemisphere. The reprocessing plants in the Northern Hemisphere are dominating the global ^{129}I inventory and more than 95% of the present mobile ^{129}I is distributed in the Northern Hemisphere (Snyder et al., 2010). Fehn and Snyder (2000) reported that the concentrations of ^{129}I in the Southern Hemisphere are lower by about two orders of magnitude than in the Northern Hemisphere.

Man-made ^{129}I was globally distributed in the environment and as a consequence the natural equilibrium isotopic $^{129}\text{I}/^{127}\text{I}$ ratios were increased by several orders of magnitude. The $^{129}\text{I}/^{127}\text{I}$ ratios in the atmosphere and in precipitation increased from a few times 10^{-12} to 10^{-9} between 1940 and 1950 in background regions of the Northern Hemisphere. In 1950, atmospheric $^{129}\text{I}/^{127}\text{I}$ ratios exceeded 10^{-9} and today they have, for instance, reached 10^{-6} such as in European seawater and north Atlantic. For more details see Yiou et al. (1994, 2002), Raisbeck et al. (1995), Fehn and Snyder (2000), Hou et al. (2002), Buraglio et al. (2000), López-Gutiérrez et al. (2004), Alfimov et al. (2004), Michel et al. (2005b, 2012),

Schnabel et al. (2007), Aldahan et al. (2007), Reithmeier et al. (2010) and Snyder et al. (2010).

The development with time of the ^{129}I deposition rates in Western Europe such as in Germany and Switzerland are known from the analyses of an alpine ice core and from direct measurements; see Michel et al. (2005b, 2012) for data and further references. The ^{129}I deposition rates derived from the Fiescherhorn ice core (Wagner et al., 1996) do not show a prominent bomb peak as for instance observed for ^{36}Cl and ^{137}Cs in the same ice core (Synal et al., 1990). Up to now, only one profile of Mississippi River Delta sediments showed a “bomb peak” for ^{129}I on the Northern Hemisphere, in parallel with one of plutonium isotopes (Oktay et al., 2000). However, due to the complex and unknown input function of these sediments no total deposition inventory of the “bomb peak” was estimated by these authors.

Due to the releases pattern, atmospheric isotopic ratios and ^{129}I deposition rates continued to increase in Europe until the end of the 1980s. Since then, ratios of nearly 10^{-6} were observed in Germany and Switzerland and remained quite constant until today (Ernst, 2003; Ernst et al., 2003; Michel et al., 2005b, 2012). The fall-out of the Chernobyl accident, mainly by wet deposition, was just a short-term episode with a highest measured $^{129}\text{I}/^{127}\text{I}$ ratio of nearly 10^{-5} (Paul et al., 1987). Englund et al. (2008) investigated a sediment profile from Sweden in an area highly contaminated by Chernobyl fall-out, but because of the dominating signal from the reprocessing plants the Chernobyl contribution to ^{129}I was not as clear as in the case of ^{137}Cs . Nowadays the North Sea appears to be the dominant source of air-borne iodine in Northern Europe due to the emissions of European reprocessing plants (Michel et al., 2005b, 2012; Nies et al., 2010).

In contrast to ^{129}I , the natural production of ^{137}Cs ($t_{1/2} = 30.07$ Ma) by spontaneous fission does not cause any significant natural abundances in the atmosphere, hydrosphere or biosphere because of its relatively short half-life. Man-made ^{137}Cs , however, has an important impact on the human environment. It started with the atmospheric explosions of atomic bombs which released about 948 PBq ^{137}Cs (UNSCEAR, 2000). During the Chernobyl accident 85 PBq ^{137}Cs were set free (UNSCEAR, 2011). The releases of ^{137}Cs from reprocessing plants are comparably low and those from nuclear power plants in normal operation even negligible. Releases of ^{137}Cs from Sellafield and La Hague were mainly marine ones: 1 PBq from La Hague and 41 PBq from Sellafield until 2005 (OSPAR, 2008). Atmospheric releases of ^{137}Cs from La Hague were less than 1 GBq for La Hague and less than 3.4 TBq for Sellafield up to 1997 (UNSCEAR, 2000, Annex C). Data of ^{137}Cs releases into the atmosphere for other reprocessing plants are not available. Also for nuclear power plants in normal operation no comprehensive data on releases into the atmosphere exist. Upper limits of ^{137}Cs releases can, however, be estimated from the release data for radioactivity bound to particulates demonstrating their insignificance. The geometric mean of the normalised release of particulate bound radioactivity is about 10^{-2} GBq/GWa to a few times 10^{-1} GBq/GWa (UNSCEAR, 2000, Annex C). Therefore, we can restrict our discussion on ^{137}Cs from atmospheric explosions and from the Chernobyl accident.

^{137}Cs – as well as ^{129}I – from the atomic explosions was globally distributed by stratospheric transport and deposited by long-term fall-out. Due to the global atmospheric transport processes (UNSCEAR, 1982) the bomb fall-out depended strongly on the geographical latitude. Decay corrected to 1981, the bomb fall-out of ^{137}Cs was about 5 kBq m^{-2} at northern latitudes between 40° and 60° and about a factor of 5 lower at the same southern latitudes. According to UNSCEAR (1982) about 25% of the global ^{137}Cs fall-out was deposited on the Southern Hemisphere. Schuller et al. (2002) measured deposition densities of ^{137}Cs in Chilean soils between 0.5 kBq m^{-2} and 5.4 kBq m^{-2} , the latter figure being surprisingly

high considering the estimates given in UNSCEAR (1982). Also the activities of ^{137}Cs in surface water differ on the Northern and Southern Hemispheres with ranges of $2.5\text{--}5 \text{ Bq m}^{-3}$ and $0.1\text{--}2 \text{ Bq m}^{-3}$, respectively (Anonymous, 1993; Nies et al., 2010).

The ^{137}Cs released from the Chernobyl accident was spread all over Europe and was detectable over the entire Northern Hemisphere. Due to tropospheric transport and a strong influence of the weather conditions, the Chernobyl fall-out was extremely inhomogeneous over Europe (De Cort et al., 1998; UNSCEAR, 2000). In southern Germany heavy local rains caused small scale depositions of up to 100 kBq m^{-2} , while in northern Germany it was just about 5 kBq m^{-2} on the average (SSK, 1996). ^{137}Cs , in contrast to ^{129}I , is one of the relatively few man-made radionuclides which are of radiological concern being a nuclide which caused and still causes significant external and internal radiation exposures of humans. ^{129}I is presently not of radiological concern, spare the direct vicinities of release points (Schmidt et al., 1998).

The radioecological settings in Germany and Chile are different. The Southern Hemisphere nearly exclusively got the radioactive fall-out, both of ^{137}Cs and ^{129}I , from the atmospheric nuclear explosions. In Germany, in addition to the weapons fall-out, the Chernobyl accident contributed significantly to the ^{137}Cs contamination. The majority of the ^{129}I fall-out in Europe stems from the releases of the European reprocessing plants, mainly from La Hague and Sellafield. Because of the high contamination of Europe due to the releases from the European reprocessing plants and because the $^{129}\text{I}/^{131}\text{I}$ isotopic ratio in the Chernobyl fall-out was determined to be 12 ± 3 , corresponding to an activity ratio $A(^{131}\text{I})/A(^{129}\text{I}) = 5.9 \times 10^7$ (Michel et al., 2005a), the contribution to ^{129}I from Chernobyl is detectable only in the highly contaminated regions in Belorussia, Russia and Ukraine, (Michel et al., 2005a) and references therein, though some indications, but no significant detection of a contribution from Chernobyl exist in highly contaminated areas of Sweden (Englund et al., 2008).

Moreover, the time scales of the different types of fall-out differ: the weapons fall-out had a broad maximum in the 1960s and decreased strongly after the Partial Test Ban Treaty in 1963, the fall-out from the Chernobyl accident was a short-term event in 1986, and the releases from the reprocessing plants increased continuously since the 1960s and reached their present, relatively stable maximum during the 1990s. Moreover, there was no ^{137}Cs fall-out before 1945, while there was continuous fall-out of iodine isotopes with an isotopic ratio of $\sim 10^{-12}$ all the time before. All these different sources of fall-out, their absolute amounts and time scales, find their expression in the depth distributions of ^{137}Cs and ^{129}I in the soils.

^{137}Cs is a dominant source of the human radiation exposure after nuclear accidents, like in Chernobyl and Fukushima. Investigations of ^{137}Cs in soils give direct clues to the expected external and internal radiation exposure of humans living on the soils. The transfer of ^{137}Cs into the food chain depends strongly on the composition of the soil and on the migration behaviour of ^{137}Cs in the soil. Therefore, the investigation of ^{137}Cs in soils has become a backbone of radioecology and radiological protection.

The relevance of investigating stable and long-lived iodine isotopes in soils for radioecology and radiological protection is not so self-evident. But, for several reasons it is of interest. First, the investigation of soil profiles gives us clues about the complex migration behaviour of ^{127}I and ^{129}I which is not finally understood (Robens and Aumann, 1988; Rao and Fehn, 1999; Ernst et al., 2003; Muramatsu et al., 2004) and the environmental behaviour of ^{129}I is important with respect to the safety assessment of long-term storage of nuclear waste in the geosphere. Second, the depth distribution of ^{127}I in soils is of interest with respect to the dependence of the iodine balance on vegetation cover, soil types and characteristics. Thirdly, the investigation of pre-nuclear soils

can give information on the natural $^{129}\text{I}/^{127}\text{I}$ ratios in the terrestrial biosphere. Finally, data on ^{129}I in soils are useful to derive and interpret integral deposition densities which are needed as a basis of retrospective dosimetry of ^{131}I after nuclear accidents; (Michel et al., 2005a) and references therein.

The purpose of this study was to measure depth-dependent concentrations and the inventories of ^{127}I , ^{129}I , and ^{137}Cs in soil profiles from Germany and Chile, to compare the human impact on the environment of the Northern and Southern hemisphere and to shed some light on the different migration behaviour of the three nuclides.

2. Experimental

2.1. Sampling and materials

Five soil profiles were taken during the summers of 1998 and 1999 from Bavaria in Southern Germany. Soil samples were collected from undisturbed coniferous and deciduous forest stands and adjacent grassland in Bavaria (Table 1). The soils were a hypolegic cambisol at Untereichet 1, a simillegic (pseudogley) at Untereichet 2, a dystrophic cambisol at Wald-Kraiburg, a hypoluvic arenol at Salzburghofer, and a fibric histosol (an upland moor under grassland) at Petting. On each site, approximately 2–3 kg of soil were taken from the humus layers and from successive soil layers in cm: 0–2, 2–4, 4–6, 6–10, 10–15, 15–20, 20–25, 25–30, 30–40, 40–50. At each studied location from Bavaria five cores covering an area of $50\text{--}100 \text{ m}^2$ were drilled and then mixed together in order to obtain a single representative profile. Kruse-Irmer and Giani (2003) performed the sampling and analysed the samples for the vertical distribution and bioavailability of ^{137}Cs in organic and mineral soils.

From Chile, eight soil profiles were taken in 1995, 1999 and 2003 in the context a series of investigations of ^{137}Cs in the Chilean environment (Schuller et al., 1997, 2004). Two of the profiles were from Easter Island with soil layers in cm: 0–3, 3–6, 6–9, 9–12, 12–15, 15–18, 18–21, 21–24, 24–27, 27–30, four from Central Chile with soil layers in cm: 0–1, 1–2, 2–3, 3–5, 5–10, 10–15, 15–20, 20–25, 25–40, 40–60, 60–80. Two soil profiles were taken from Antarctica Chile (Bridgeman Islands) in 1995 with soil layers in cm: 0–2, 2–3, 3–4, 4–5, 5–6, 6–8. The different depths of the Chilean soil profiles depended on the depths of the soil columns available at the different locations. Details on the sampling locations and on some physicochemical properties of the soils are given in Table 1.

2.2. Analytical procedures

For the ^{127}I , ^{129}I and ^{137}Cs analyses, the soil samples were air-dried and sieved $<2 \text{ mm}$. Soil physicochemical properties (organic matter, pH, clay content, iron and aluminium oxide) were determined using standard methods as described by Schlichting et al. (1995) at the Institute of Soil Science, Leibniz University Hannover. Soil pH was determined with pH-metre in a 1:2.5 suspension of CaCl_2 0.01 M. Organic matter was determined by direct oxidation with air at 600°C . From the difference between weight of soil before and after the oxidation the amount of organic matter was estimated. For the determination of clay content, the soil samples were mixed with hydrogen peroxide and heated to decompose the organic matter. After dispersion with meta-phosphate the determination of the clay content (particle diameters $<2 \mu\text{m}$) was carried out using standard Stoke's law sedimentation technique. Active iron and aluminium oxides were extracted with oxalate-solution and was determined by atomic absorption spectrometry.

Table 1

Locations and physicochemical properties of the investigated soils.

Sampling location	Sampling date	Latitude longitude	Altitude in m	Soil type	Depth in cm	pH [CaCl ₂]	Organic matter %	Clay content ^a %
Bavaria, Germany Wald-Kraiburg	01.08.98	48°13'0"N 12°26'0"E	424	Dystric cambisol	8	3.1	19.6	11.2
		47°51'0"N 12°58'0"E			15	4.0	4.0	17.7
Untereichet 1	01.09.99	47°51'0"N 12°58'0"E	418	Pseudogley cambisol	28	5.4	9.1	23.3
		47°52'0"N 12°58'0"E			50	6.1	5.0	28.0
Untereichet 2	01.09.99	47°52'0"N 12°58'0"E	418	Hypogleyic cambisol	4	3.7	17.2	21.5
		47°51'0"N 13°0'0"E			50	3.9	5.9	25.8
Salzburghofer	01.09.99	47°51'0"N 13°0'0"E	410	Hypoluvic arenosol	18	7.0	6.3	8.5
		47°52'0"E			32	7.1	3.3	6.9
Petting	01.09.99	47°53'0"N 12°52'0"E	450	Fibric histosol	50	7.1	1.9	9.3
		47°52'0"E			25	3.6	78.9	2.2
Antarctica Lado Pinguinera	10.01.95	62°09'0"S 58°29'0"W	—	—	8	3.9	8.8	4.4
		62°09'0"S 58°29'0"W			8	3.7	6.7	4.3
Central Chile Curinanco Alto	18.11.99	39°41'18"S 73°57'6"W	750	Hapludant	03–05	4.1	11.18	29.2
		39°44'30"S 73°22'48"W			20–25	4.3	22.38	17.6
Curinanco Bajo 1	16.11.99	39°44'30"S 73°22'48"W	30	Palehumult	03–05	4.5	17.58	22.6
		39°44'30"S 73°22'48"W			20–25	4.8	10.36	8.6
Curinanco Bajo 2	12.12.03	39°44'30"S 73°22'48"W	30	Palehumult	03–05	4.6	17.1	23.5
		38°41'30"S 72°53'0"W			20–25	4.7	9.96	6.8
Coastal Cordillera	09.01.03	38°41'30"S 109°30'0"W	75	Palehumult	03–05	4.9	8.78	35.6
		38°41'30"S 109°30'0"W			20–25	5.0	3.58	53.9
Easter Island Easter Island 1	10.01.03	27°6'0"S 109°30'0"W	—	—	06–09	4.5	10.78	9.0
		27°6'0"S 109°30'0"W			27–30	4.4	6.26	4.1
Easter Island 2	10.01.03	27°6'0"S 109°30'0"W	—	—	06–09	4.7	5.9	5.0
		27°6'0"S 109°30'0"W			27–30	5.1	4.1	5.1

—Not observable at the sites.

^a Attributed to the total soil, including organic matter and all mineral components.

The γ -spectrometric ¹³⁷Cs measurements were carried out using three high-purity Ge detectors with relative efficiencies of 30%, 60%, and 50% at IRS in Hannover. The detectors were mounted in lead shields and coupled with multi-channel analysers. Measurement-times of between 24 h and 72 h (depending on activity and mass of the samples) guaranteed relative uncertainties of less than 5% for most of the samples.

Iodine was separated from the soils following a method described by Schmidt et al. (1998). This method was based on dry combustion with excess oxygen and nitrogen. The gaseous iodine was collected in an alkaline hydrogensulfite solution. The combustion apparatus consisted of two telescoped quartz pipes with feeders for oxygen and nitrogen. The samples together with ¹²⁵I yield tracer were placed in the inner pipe and heated first with a Bunsen burner. Then the inner quartz pipes were slowly and cautiously shoved into a pipe oven and heated to 1200 °C. Typical yields were between 70% and 96%. The chemical yields and the concentrations of ¹²⁷I and ¹²⁹I were determined using aliquots of the alkaline hydrogensulfite solution.

For measurement of ¹²⁹I, the iodine was precipitated with stable iodine carrier (Woodward iodine) as silver iodide. Then, 1 mg of AgI was mixed with 4 mg silver and pressed into sample holders to be used as AMS-targets.

¹²⁹I was measured by accelerator mass spectrometry (AMS) at the PSI/ETH AMS facility at ETH Hönggerberg, Zurich, Switzerland using the PSI/ETH 0.5 MV tandem accelerator "Tandy". The selected charge state was 4⁺ resulting in the total energy of 2.5 MeV (Stocker et al., 2005). The m/q interference ⁹⁷Mo⁴³ was well-separated in the most of the measured ΔE - E_{res} spectra. However, some measurements were dismissed due to high intensity of the sample-specific Mo background. With the exception of few low-level samples, the

statistics was limited by ~4% reproducibility of single cathodes. The ¹²⁹I/¹²⁷I machine background was $(3\text{--}5) \times 10^{-13}$ and did not influence the majority of the measurements.

The ¹²⁹I blank values of the total analyses were determined with chemically processed Woodward iodine as trace catcher. The ¹²⁹I masses and ¹²⁹I/¹²⁷I ratios in the blanks per analysis were 2 fg and 7 fg, respectively, $(2.5 \times 2.1^{\pm 1}) \times 10^{-13}$ and $(26 \times 1.8^{\pm 1}) \times 10^{-13}$ in two different laboratories used (Daraoui, 2010).

Stable iodine concentrations of aliquots of the sample solutions were determined by ICP-MS (Thermo X7) at the Institute of Inorganic Chemistry, Leibniz University Hannover using the method described by Ernst (2003) and Klipsch (2005). The ICP-MS was calibrated with standard solutions by CPI International in the Netherlands. The sample solution was diluted with tetra-methyl-ammonium hydroxide (TMAH) (10 mmol) same matrix for the iodine standard. Blank solutions of 10 mmol TMAH were analysed before any solution to ensure that memory effects were monitored. We used ¹²⁹Xe and ¹³²Xe as internal standards to monitor for drifts in machine sensitivity and operation. Standard of I⁻ concentrations (5 ng g^{-1}) was analysed before, in between and after the sample measurements.

Measurement uncertainties and characteristic limits (decision thresholds, detection limits, and coverage intervals) were determined according to GUM (ISO, 1995; JCGM, 2008) and ISO 11929 (ISO, 2010). Typical ¹³⁷Cs, ¹²⁹I and ¹²⁷I detection limits were 0.01 Bq kg^{-1} , $0.04 \mu\text{Bq kg}^{-1}$ and 0.1 ng g^{-1} , respectively.

More detailed description of the sample preparation and the analytical techniques are given elsewhere (Schmidt et al., 1998; Szidot et al., 2000; Ernst et al., 2003; Klipsch, 2005; Daraoui, 2010).

In order to control the ¹²⁹I analyses, IAEA-Soil-375 reference material was analysed in regular intervals between the analyses of

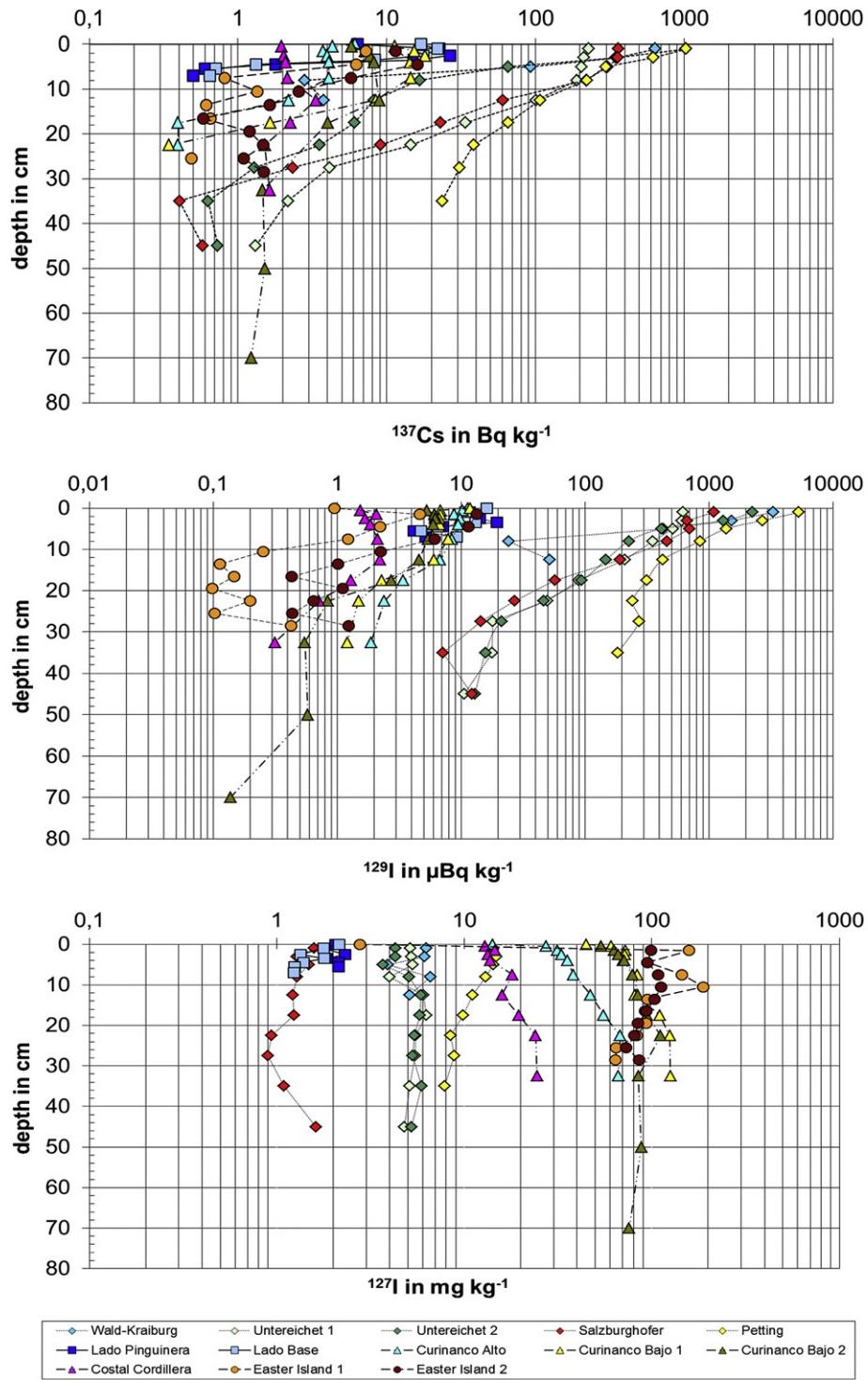


Fig. 1. Activity concentrations of ^{137}Cs and ^{129}I and concentrations of ^{127}I in the soil profiles. In the entire figures, data from Bavaria are plotted as rhomboids, those from the Easter Island as circles, from Central Chile as triangles, and from Chilean Antarctica as squares.

the soil samples. The ^{127}I was measured in 14 samples ($\sim 5 \text{ g}$ dry weight for each) and subjected to the same combustion procedure. The mean value and the standard deviation was $(1.58 \pm 0.18) \text{ mBq kg}^{-1}$. This mean value is 12% lower than the recommended value of 1.7 mBq kg^{-1} (IAEA, 2000) or 20% lower than the recommended value (2 mBq kg^{-1}) listed in the IAEA (2002) AQCS Reference Material Catalogue 2002–2003, but agrees very well with the results of $1.59 \pm 0.08 \text{ mBq kg}^{-1}$ by Jiang et al. (2005) and $1.54 \pm 0.13 \text{ mBq kg}^{-1}$ by Marchetti et al. (1997).

3. Results and discussion

The numerical results of the activity concentrations of ^{137}Cs and ^{129}I , of the concentrations of ^{127}I as well as of the soil parameters analysed, which are dealt with in this work can be obtained in a thesis of Daraoui (2010). Note, that there are different notations used in literature for ^{129}I concentrations in environmental samples: physicists tend to use the units atoms per L or kg, chemists like g g^{-1} , and radioecologists use Bq L^{-1} , Bq kg^{-1} or Bq m^{-3} . In this

paper, we discuss ^{129}I activity concentrations of soils in Bq kg^{-1} . For special comparisons, we also use the unit g g^{-1} for ^{129}I concentrations. The following conversion holds: $1 \text{ fg } ^{129}\text{I g}^{-1} = 4.67 \times 10^9 \text{ atoms kg}^{-1} = 6.54 \mu\text{Bq/kg}$.

3.1. Depth profiles of ^{137}Cs , ^{127}I , and ^{129}I

The measured depth profiles of ^{137}Cs , ^{127}I and ^{129}I are shown in Fig. 1. The activity concentrations for ^{137}Cs and ^{129}I of the topsoils differ markedly between the samples from the Northern and the Southern Hemisphere, the latter being significantly lower. However, while those differences are just about an order of magnitude in the case of ^{137}Cs , they amount to about two orders of magnitude in the case of ^{129}I .

The ^{137}Cs activity concentrations in the topsoils from Bavaria were between $(228 \pm 8) \text{ Bq kg}^{-1}$ and $(1028 \pm 33) \text{ Bq kg}^{-1}$; in the lowest layers they were between $(0.58 \pm 0.18) \text{ Bq kg}^{-1}$ and $(23.6 \pm 0.9) \text{ Bq kg}^{-1}$. In the topsoils from Chile, the ^{137}Cs activity concentrations were between $(2.0 \pm 0.2) \text{ Bq kg}^{-1}$ and $(22.6 \pm 0.7) \text{ Bq kg}^{-1}$ and between $(0.35 \pm 0.18) \text{ Bq kg}^{-1}$ and $(1.5 \pm 0.3) \text{ Bq kg}^{-1}$ in the lowest layers. The ^{129}I activity concentrations in samples from Bavaria in Germany ranged from $(0.62 \pm 0.02) \text{ mBq kg}^{-1}$ to $(5.3 \pm 0.2) \text{ mBq kg}^{-1}$ at the surfaces and $(0.18 \pm 0.01) \text{ mBq kg}^{-1}$ to $(0.011 \pm 0.001) \text{ mBq kg}^{-1}$ in the lowest layers. In the topsoils from Chile, the ^{129}I activity concentrations ranged from $(16.2 \pm 0.7) \mu\text{Bq kg}^{-1}$ to $(1.5 \pm 0.1) \mu\text{Bq kg}^{-1}$ and from $(0.14 \pm 0.11) \mu\text{Bq kg}^{-1}$ to $(9.2 \pm 0.5) \mu\text{Bq kg}^{-1}$ in the lowest layers.

Also the depth dependences of the ^{137}Cs and ^{129}I activity concentration profiles were different. In the Bavarian soils, the ^{137}Cs profiles were much steeper than in the Chilean samples, the data covering three orders of magnitude in Bavaria and just one and a half orders of magnitude in Chile. In the case of ^{129}I , the Bavarian profiles are also steeper than the Chilean ones.

The individual soil characteristics, in addition, influence the profiles as can be seen in the differences among the profiles from Bavaria and Chile. There are large differences among the ^{137}Cs profiles from Bavaria. The mobility of ^{137}Cs was lower in mineral soils, as in the profiles from Untereichet, Wald-Kraiburg and Salzburghofer, compared to organic soils, e.g. the profile from Petting. The highest ^{137}Cs activities were located in the upper 10 cm of the soils (Untereichet 2, Wald-Kraiburg and Salzburghofer). The low mobility of ^{137}Cs was due to specific sorption and fixation of ^{137}Cs by expandable clay minerals. The samples from Untereichet and Wald-Kraiburg had higher clay contents than the other soils (Table 1). But, the samples of Untereichet 1 and 2 have same clay content but different pH values. Therefore the ^{137}Cs profile of Untereichet 2 was much steeper than in the Untereichet 1. The adsorption of ^{137}Cs depended not only on the clay, but also on the cationic exchange capacity (CEC), pH of the soil and the organic matter. The upland moor soil of Petting had higher organic matter content and lower clay content than the mineral soils. Therefore, the ^{137}Cs profile of Petting is less steep than the other ones. The adsorption of ^{137}Cs at organic matter is regarded to be unspecific and rather weak, so that the organic matter is assumed to enhance ^{137}Cs mobility in soils, see Dumat and Staunton (1999) and Kruse-Irmer and Giani (2003) for a summary of some of these recent findings.

In the Chilean profiles, the ^{137}Cs activities were less steep than in the profiles from Bavaria and are nearly constant with depth (0–10 cm). The samples from Central Chile had higher organic matter and clay contents than those from Antarctica and Easter Island (Table 1).

The sample from Antarctica (polar climate) had a maximum 27 Bq kg^{-1} of ^{137}Cs activity in the topsoil. The lowest ^{137}Cs activities in the samples from Central Chile were in the soil from Coastal

Cordillera with value 2 Bq kg^{-1} . The four regions in Central Chile have a moderately warm summer climate with rainy winters (Schuller et al., 2002). On the Ester Island (tropical climate) the results showed higher concentrations in the humus ($6\text{--}14 \text{ Bq kg}^{-1}$) than in the rest of the profiles (just 2 Bq kg^{-1}).

For ^{129}I , the steepest profiles tended to be found in those soils with the lowest stable iodine concentrations, while those with high stable iodine concentrations tended to exhibit the flattest profiles, as it was also observed by Ernst, 2003 (Ernst et al., 2003). For given fall-out situation regarding its absolute deposition density and time scale, a flat profile means that the radionuclides migrated quickly and that there was little adsorption capacity, while a steep one indicates a slow migration and a high adsorption capacity. As shown in Fig. 1 for the samples from Bavaria, the ^{129}I activities were found to decrease exponentially with depth, but not so clearly for the samples from Chile. The ^{129}I activities measured in the depth profiles span nearly two to three orders of magnitude, ranging from $7.2 \mu\text{Bq kg}^{-1}$ to $5326 \mu\text{Bq kg}^{-1}$ in the soils from Bavaria and from $0.1 \mu\text{Bq kg}^{-1}$ to $19 \mu\text{Bq kg}^{-1}$ in the soils from Chile. As for ^{137}Cs , the migration of ^{129}I was lower in mineral soils than in organic soils from Bavaria.

Generally, at all locations the ^{127}I concentrations were fairly constant with depth as a consequence of a long-term equilibrium between atmospheric input and exchange processes between soil components and surface and groundwater. Ernst et al. (2003) concluded that the iodine inventories in soils from Lower Saxony in Germany are the result of millennia-long atmospheric input at low deposition rates.

There were, however, dramatic differences in the absolute ^{127}I concentrations in the soils at the different locations with a total range between 1 mg kg^{-1} and 200 mg kg^{-1} . The ^{127}I concentrations in Bavaria were relatively low, the concentrations from the Central Chile and from the Easter Island much higher. The samples from Antarctica exhibit the lowest concentrations of $1\text{--}2 \text{ mg kg}^{-1}$ together with the samples from Salzburghofer in Bavaria. In all the German samples, the ^{127}I concentration were below 20 mg kg^{-1} , the highest ones were found in the upland moor soil of Petting. The lowest ^{127}I concentrations in the samples from Central Chile were in the soil from the Coastal Cordillera with values between 12 mg kg^{-1} and 25 mg kg^{-1} . The rest of the samples from the Central Chile and from the Easter Island had concentrations between 30 mg kg^{-1} and 200 mg kg^{-1} with one exception: the humus sample from Curinanco Alto just contained 14 mg kg^{-1} iodine.

These large differences in the iodine concentrations can be understood when looking to the input pathway of iodine into the soils. Iodine in the soils originates mainly from the oceans, where it is released from the ocean surface, transported over the continents and brought to the surface by wet and dry deposition. Generally, wet deposition is assumed to be more effective for deposition and, thus, the influx of iodine to the surface should scale with the annual precipitation. In addition, there will be some temperature effect on the evaporation of iodine from the ocean surface and on the biomasses producing CH_3I .

Bavaria has a temperate climate and is located far away from the sea in the transition zone of the maritime climate of Western Europe and the continental climate in Eastern Europe. The mean annual precipitation in the sampling region of Bavaria is $800\text{--}900 \text{ mm}$.

The samples from the Central Chile come from the region of Valdivia which has a temperate oceanic climate with a mean annual precipitation of 2700 mm . Here the Andean Cordillera intercepts moist westerly winds along the Pacific coast during winter and summer months; these winds cool as they ascend the mountains, creating heavy rainfall on the west-facing slopes of the mountains. The northward-flowing oceanic Humboldt Current creates humid

and foggy conditions near the coast. The Easter Island has a subtropical maritime climate with a mean annual precipitation of about 1100 mm. At the Bridgeman Islands in the Chilean Antarctica the mean annual precipitation just exceeds 600 mm in an arctic climate.

The high iodine concentrations in the samples from Central Chile and from the Easter Island are an expression of the high oceanic influence and the high precipitation rates, while Bavaria has to be regarded as an iodine-deficient region. The conditions in Antarctica together with low precipitation rates were the reason for the observed low iodine concentrations in the soils.

3.2. $^{127}\text{I}/^{129}\text{I}$ isotopic ratios

In the introduction it was stated that in the pre-nuclear global system, the natural ^{129}I and ^{127}I in the mobile iodine inventory are in equilibrium. This can certainly be assumed for the atmosphere and the maritime hydrosphere. Further, in our previous studies on ^{129}I in Western Europe and Germany (Michel et al., 2012) it was frequently stated that the man-made ^{129}I enters the natural iodine cycle and that therefore it is meaningful to look at the ^{129}I data in form of the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios. Given, however, the different sources and fall-out histories of natural and man-made ^{129}I in so different geographical regions, in the present study the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios alone do not give clear-cut answers on the human impact.

The $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in the soil profiles investigated spanned an extreme range of five orders of magnitude from less than 10^{-12} to more than 10^{-7} (Fig. 2). The differences between the Bavarian and Chilean soils were larger than seen in the ^{129}I activity concentrations because the lower contaminations in the Southern Hemisphere go in parallel with higher stable iodine concentrations in the samples from Central Chile and from the Easter Island. The precipitation in the Southern Hemisphere can today be assumed to have $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of the order of 10^{-10} ; i.e. the $^{129}\text{I}/^{127}\text{I}$ isotopic ratio in surface waters of the ocean far away of release points (Kilius et al., 1994; Yiu et al., 1994). In Germany, the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of precipitation are today in the range of 10^{-7} – 10^{-6} and in soils with low stable iodine concentrations $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of 10^{-7} are frequently observed in topsoils of Northern Germany (Michel et al., 2004, 2012). Thus, the $^{129}\text{I}/^{127}\text{I}$ isotopic

ratios of 10^{-8} – 10^{-9} observed in this work in the topsoils from Bavaria, which is more distant from the North Sea than Northern Germany, are well in line with the earlier observations.

The $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in the soils from the Central Chile and from the Easter Island ranged in the topsoils only between 0.2×10^{-12} and 10^{-10} . The data for the Central Chile were slightly higher than those for the Easter Island, which might be due to the higher precipitation rate at the coast of Central Chile and to the recent additional influx of iodine with $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of 10^{-10} .

In the samples from the Easter Islands, for the first time, $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of 10^{-12} and below were observed in the pedosphere. They can be interpreted as representing the global pre-nuclear equilibrium ratio. The observation of $^{129}\text{I}/^{127}\text{I}$ isotopic ratios as low as 0.2×10^{-12} in the profiles from the Easter Islands and the results obtained by Ernst (2003) for “pre-nuclear” iodine preparations of $(0.2 \times 1.4^{+1}) \times 10^{-12}$ shed some doubt on whether or not today's “standard” natural equilibrium $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of $\sim 1.5 \times 10^{-12}$ (Fehn et al., 1986; Schink et al., 1995; Moran et al., 1998) might be too high.

The lowest isotopic ratios at depth measured in the German soils exceeded the pre-nuclear equilibrium ratios by more than two orders of magnitude, as well as the lowest ratio measured so far in a pre-nuclear soil of $(5.7 \pm 1.1) \times 10^{-12}$ (Szidat et al., 2000).

It is a remarkable fact that the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in the two soil profiles from Antarctica are nearly constant with ratios between 3×10^{-10} and 10^{-9} . These relatively high isotopic ratios are to be attributed to the low stable iodine in these soils. Evidently, equilibrium conditions do not exist between the old, pre-nuclear iodine and the modern one.

It has been found useful to look at the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios as a function of ^{129}I and ^{127}I , respectively (Michel et al., 2005b, 2012). Such presentations allow demonstrating the disequilibria which exist today between the mainly old, natural ^{127}I and the recent, man-made ^{129}I in the different environmental materials.

It was observed (Michel et al., 2012; Nies et al., 2010) that the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in oceanic seawater from the North Sea, the Northeast Atlantic, the Indian Ocean, and the Pacific nearly exclusively depend on the admixture of man-made ^{129}I , the stable ^{127}I being fairly constant (40 ± 9) ng g⁻¹. The correlation between $^{129}\text{I}/^{127}\text{I}$ isotopic ratios and the ^{129}I concentration is shown in Fig. 3

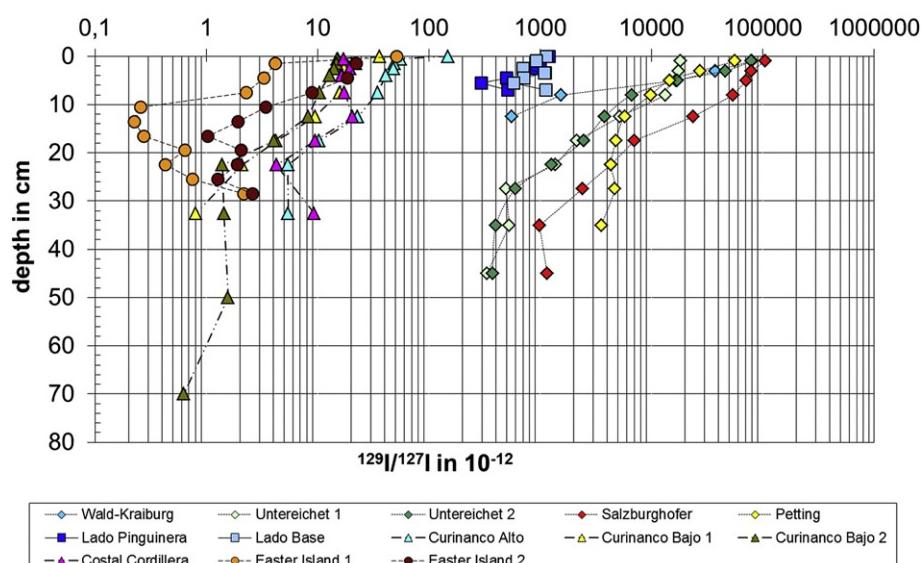


Fig. 2. The depth dependence of $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in the soil profiles.

together with the results of this work. Deviations from the strict correlation are seen in European seawater only for samples from estuaries and the Baltic Sea which are influenced by freshwater or from the German tideland (Michel et al., 2012; Nies et al., 2010).

The pre-nuclear situation in the oceanic seawater is presently assumed to be characterised by an $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of $\sim 1.5 \times 10^{-12}$ which with an ^{127}I concentration of 39 ng g^{-1} yields a pre-nuclear ^{129}I concentration of $5.8 \times 10^{-20} \text{ g g}^{-1}$ (Fig. 3). The highest $^{129}\text{I}/^{127}\text{I}$ isotopic ratios observed so far showed ^{127}I isotopic ratios of 3×10^{-6} close to the outlets of Sellafield and La Hague; six orders of magnitude higher than the pre-nuclear equilibrium isotopic ratio.

As stated before, the samples investigated in this work covered quite different fall-out scenarios and consequently the dependence of the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios on the ^{127}I and ^{129}I concentrations is rather complicated. The ^{127}I data cover two orders of magnitude, the Chilean data being about an order of magnitude higher than the German ones. The only exception to this is the humus sample from Easter Island 1. Also the samples from Antarctica are special due to their particularly low ^{127}I concentrations. There is no correlation between the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios and the ^{127}I concentrations.

The ^{127}I concentrations are relatively constant for each individual profile. Exceptions are the upland moor profile from Petting (D) and the Curinanco Alto profile from Chile. In Petting, the upper samples were higher by a factor of three than the lower ones. At Curinanco Alto, the ^{127}I concentrations increased with depth by a factor of three. There was a general tendency in the ^{127}I profiles from Central Chile that the ^{127}I concentrations increased with depth. This was not the case in the Bavarian samples. The lower ^{127}I concentrations at the surface may be a consequence of the heavy rainfalls with higher run-off and washout than in more moderate climates. Thus, the ^{127}I concentrations are, at first hand, the result of different climatic conditions; at second hand they reveal the individual soil properties.

For ^{129}I , the profile data plot in general parallel to the correlation line of the oceanic seawater, the data from Germany being roughly displaced by two orders of magnitude to higher $^{129}\text{I}/^{127}\text{I}$ isotopic ratios relative to those from Chile. This means that the iodine in the soils was simply an admixture of a seawater related component to the old pre-nuclear iodine in the samples. Similar behaviour was already observed for precipitation, surface and groundwater in Northern Germany (Michel et al., 2005b, 2012; Nies et al., 2010). The different patterns of the data in the two parts of Fig. 3 clearly

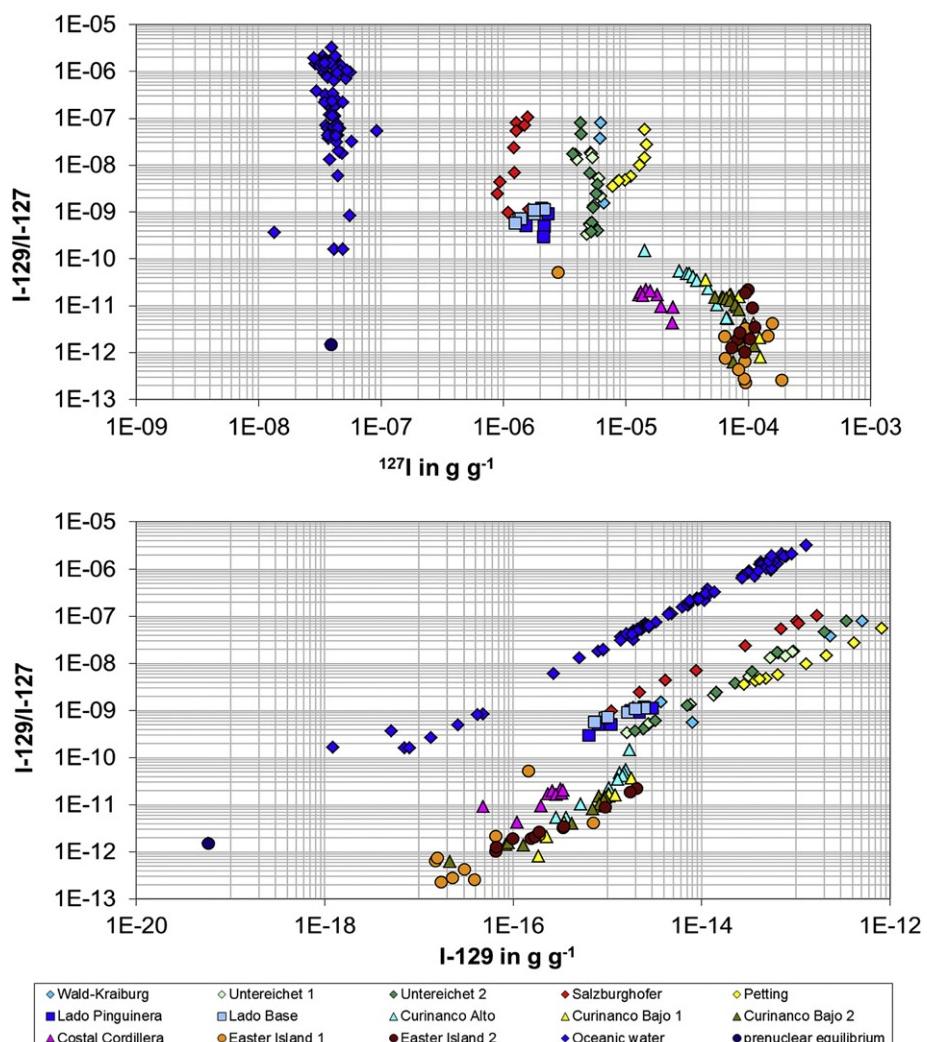


Fig. 3. The dependence of $^{129}\text{I}/^{127}\text{I}$ isotopic ratios on ^{127}I concentrations (top) and on ^{129}I concentrations (bottom) in the soil profiles analysed in this work and in oceanic seawater from (Michel et al., 2012; Nies et al., 2010).

demonstrate the disequilibrium of ^{127}I and ^{129}I in the different environmental compartments.

3.3. Integral deposition densities of ^{137}Cs , ^{127}I and ^{129}I

Since the majority both of ^{137}Cs and modern ^{129}I is still retained in the upper 30 cm of the soil profiles, integration over the concentration data allowed calculation of the inventories of ^{137}Cs and ^{129}I in units of mBq m^{-2} and kBq m^{-2} , respectively, according to equation (1). For each layer of the profiles the “deposition density” or inventory $D(d_1, d_2)$ contained in the layer with depth between d_1 and d_2 is calculated by

$$D(d_1, d_2) = \int_{d_1}^{d_2} C(d) \cdot \rho(d) dd. \quad (1)$$

$C(d)$ being the specific activity or mass concentration at depth of ^{137}Cs and ^{129}I , respectively, and $\rho(d)$ the bulk density of the air-dried soil at depth d . The total inventory D in a soil profile with the maximum sampling depth d_{\max} is then $D(0, d_{\max})$. Equation (1) does not take into account any losses into the groundwater, resuspension, evapotranspiration, soil erosion, vegetation intake, but represent the amounts found at the time of sampling the soils.

For ^{127}I , deposition densities and inventories in units of g m^{-2} calculated according to equation (1) cannot be regarded as archives. Rather, these inventories represent the equilibrium amount of ^{127}I per unit area as a consequence of a long-term long fall-out history with a historical development of the soils and a complex history of exchange with surface water and biospheric materials. However, the ^{127}I inventories in soil profiles of comparable depths give clues about the availability of the essential trace element iodine in the respective regions depending on the soil properties.

Since all or an overwhelming part of the ^{137}Cs and ^{129}I was brought into the soils during the last 50 years and since most of the radionuclides is still located in the upper parts of the soil profiles, the inventories can be assumed to represent archives of the fall-out history. This is beyond reasonable doubt in the case of ^{137}Cs . For ^{129}I it is not so obvious though the ^{129}I profiles strongly decrease and more than 90% of the total ^{129}I was located in the upper 20 cm in the soils, both for Bavaria and Chile. But, about 4–8% of the total ^{129}I was located in the below 20 cm in the soils from Chile and only 1–3% in the soils from Bavaria. Generally, the profiles from Chile are flatter than those from Bavaria, pointing to a longer migration history. But even in 2 m deep soil profiles from Northern Germany, $^{129}\text{I}/^{127}\text{I}$ isotopic did not go below 10^{-10} (Ernst et al., 2003). This demonstrated that man-made ^{129}I had already reached depths below 2 m. How large the loss of ^{129}I by fast and deep migration has been is not clear, as well as the sorption mechanism of the iodine isotopes; see Ernst (2003) for a more detailed discussion. In Fig. 4, we have plotted the ^{137}Cs and ^{129}I inventories as a function of the lower integration limiting depth and in Table 2 we present the inventories in numerical form.

The slopes of the inventories of ^{137}Cs and ^{129}I in Fig. 4 exhibit some differences which are multifactorial and can only be explained qualitatively. The slopes are influenced by the duration of the fall-out histories, the climatic conditions, by the chemical properties of iodine and caesium and the properties of the individual soils. The flatter the profiles are, the more of the radionuclide has migrated into deeper depths.

Since it is scarcely possible to distinguish the slopes by the naked eye, we have plotted the ratios of the inventories, $D(d, d_{\max}) / (^{129}\text{I})/D(d, d_{\max}) (^{137}\text{Cs})$, also in Fig. 4. If the ratios increase with depth, ^{129}I migrated faster than ^{137}Cs and vice versa. This plot gives a surprising result. In most of the soil profiles, ^{129}I has migrated faster than ^{137}Cs , as one would have expected, but not in all. In the

profile Easter Island 2 the two nuclides were equally fast, in the profiles Coastal Cordillera and Curinanco Bajo 2 ^{137}Cs migrated faster than ^{129}I . From the soil properties, we have no explanation of these facts.

The ^{137}Cs inventories in the soils from Bavaria ranged from 22 kBq m^{-2} in dystrophic cambisol at Wald-Kraiburg to 62 kBq m^{-2} in upland moor under grassland at Petting with geometric mean of $(41 \times 1.4^{\pm 1}) \text{ kBq m}^{-2}$. In Chile the geometric mean for ^{137}Cs was only $(1.7 \times 2.0^{\pm 1}) \text{ kBq m}^{-2}$. The Bavarian profiles are strongly affected by Chernobyl fall-out, while for the profiles from Chile neither a significant contribution from Chernobyl is seen nor has to be assumed. The ^{137}Cs inventories ranged between 0.64 kBq m^{-2} in the samples from the Easter Islands and 3.74 kBq m^{-2} in Central Chile.

The ^{129}I , the inventories in Bavaria ranged between 81 mBq m^{-2} in an eutrophic cambisol at Untereichet 1 and 220 mBq m^{-2} in an upland moor under grassland at Petting. The geometric mean of the Bavarian ^{129}I inventories was $(109 \times 1.5^{\pm 1}) \text{ mBq m}^{-2}$. We observed also a wide range of values of ^{129}I inventories in all the Chilean samples from 0.12 mBq m^{-2} to 1.7 mBq m^{-2} , with a geometric mean of $(1 \times 1.9^{\pm 1}) \text{ mBq m}^{-2}$. Thus, the ^{129}I inventories from Bavaria are about 100 times higher than in Chile. The high ^{129}I inventories in the soils from Bavaria are due to the releases from the European reprocessing plants La Hague and Sellafield. The liquid releases into the Irish Sea and the English Channel, the marine transport and the transition of iodine into the atmosphere and into precipitation dominate the pathway of the ^{129}I into the continent (Michel et al., 2012).

The ^{127}I and ^{129}I inventories in the depth profiles from Lower Saxony of $(3.5 \times 1.6^{\pm 1}) \text{ g m}^{-2}$ and $(168 \times 1.5^{\pm 1}) \text{ mBq m}^{-2}$, respectively, measured by Ernst et al. (2003) are slightly higher than those measured in this work in the samples from Bavaria, which showed $(2.2 \times 1.8^{\pm 1}) \text{ g m}^{-2}$ and $(109 \times 1.5^{\pm 1}) \text{ mBq m}^{-2}$, respectively. However, the differences between the ^{129}I inventories in Bavaria and Northern Germany are not significant. There is one other determination by Schnell (1997) who measured $(1.4 \times 1.8^{\pm 1}) \text{ g m}^{-2}$ and $(329 \times 2.4^{\pm 1}) \text{ mBq m}^{-2}$, respectively, for the ^{127}I and ^{129}I inventories at 12 different locations Germany. We cannot explain the relatively high ^{129}I inventory observed by Schnell (1997).

For ^{127}I , the inventories in Bavaria are consistently lower than in Lower Saxony, which can be explained by the larger distance from the sea. Generally, one expects that ^{127}I and ^{129}I will decrease if one goes east over the European continent. This was confirmed by ^{127}I and ^{129}I inventories measured in samples from Moscow/Russia and Zhitomir/Ukraine (Szidat et al., 2000; Michel et al., 2005a). Neither Moscow nor Zhitomir was significantly affected by fall-out from the Chernobyl accident. For ^{129}I , all these data are higher by orders of magnitude than the ^{129}I inventory measured by Szidat et al. (2000) in a pre-nuclear soil profile. It is to mention, however, that the pre-nuclear soil profile originated from a Russian Museum and that it is not clear whether the samples were free of contamination with modern ^{129}I . Thus, the ^{129}I inventory of $(0.08 \pm 0.02) \text{ mBq m}^{-2}$ can be regarded as an upper limit only.

For Northern Germany we can compare the inventories of ^{127}I and ^{129}I in the soils with the annual deposition densities of the nuclides. Ernst et al. (2003) determined $(4.0 \times 1.2^{\pm 1}) \text{ mg m}^{-2} \text{ a}^{-1}$ and $(11 \times 1.3^{\pm 1}) \text{ mBq m}^{-2} \text{ a}^{-1}$ for ^{127}I and ^{129}I , respectively, from time series of ^{127}I and ^{129}I in precipitation starting in 1997 (Szidat et al., 2000). See Daraoui (2010) and Michel et al. (2012) for more recent data. This comparison shows clearly that the stable iodine in the soils is the product of a millennia-long fall-out and consequently of the complex histories of the soils. The ^{129}I is overwhelmingly due to the fall-out history of the last 50 years. Wagner et al. (1996) observed a steady increase of the annual ^{129}I deposition rates from about $0.01 \text{ mBq m}^{-2} \text{ a}^{-1}$ to more than $10 \text{ mBq m}^{-2} \text{ a}^{-1}$.

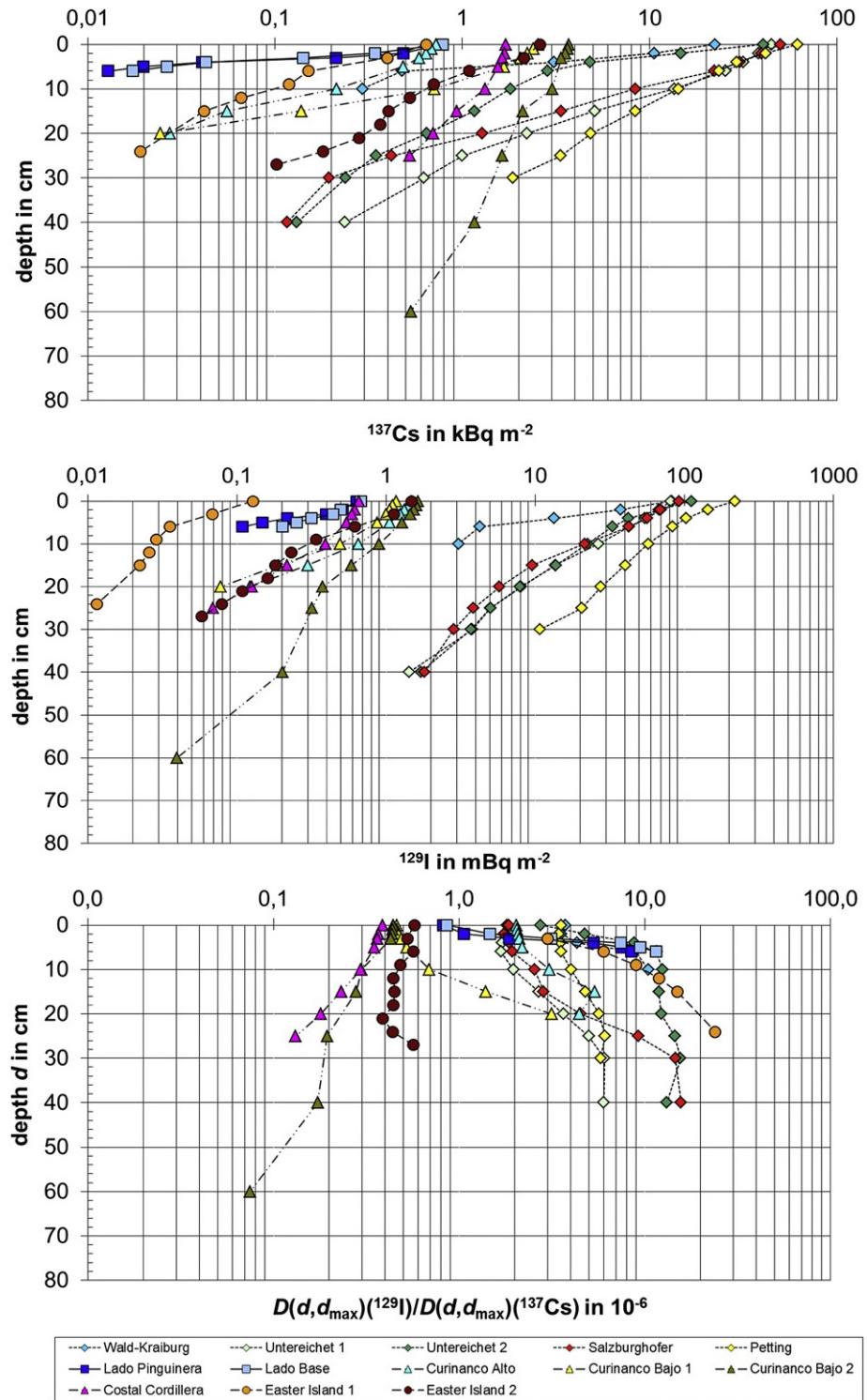


Fig. 4. Depth dependence of ^{137}Cs and of ^{129}I inventories in the soil profiles.

around the year 2000 in an ice core from the Fiescherhorn/Switzerland. After the year 2000, the annual deposition rates are fairly constant with a slightly falling tendency to the year 2005 (Michel et al., 2012).

Since the ^{129}I inventories in the soils from the Southern Hemisphere will be discussed as being proxies of the integral bomb fallout, the question for the integral deposition density of bomb ^{129}I on the Northern Hemisphere is of interest. In European archives, such as the Fiescherhorn ice core a prominent bomb peak of the annual

deposition densities was observed for the radionuclide ^{36}Cl (Synal et al., 1990). But no bomb peak is seen for ^{129}I ; the annual deposition densities of ^{129}I continue to increase after 1963 due to the onset of reprocessing and respective releases in Europe (Wagner et al., 1996; Reithmeier et al., 2006). Up to 1965, an integral ^{129}I deposition density of 0.6 mBq m^{-2} is calculated from the Fiescherhorn ice core.

In Chile, the situation is completely different. The ^{127}I inventories are more than 10-times higher than in Bavaria, but the ^{129}I

Table 2Inventories of ^{137}Cs , ^{127}I , and ^{129}I in soil profiles from the different areas.

	Precipitation in mm	$D(^{137}\text{Cs})^a$ in kBq m $^{-2}$	$D(^{127}\text{I})$ in g m $^{-2}$	$D(^{129}\text{I})$ in mBq m $^{-2}$	Reference
Central Chile 1999/2003 ($n = 4$)	1500–2300	$1.9 \times 1.8^{\pm 1}$	$24.0 \times 2.6^{\pm 1}$	$1.2 \times 1.5^{\pm 1}$	This work
Easer Island, 2003 ($n = 2$)	1100	$1.3 \times 2.7^{\pm 1}$	$34.3 \times 1.3^{\pm 1}$	$0.6 \times 3.7^{\pm 1}$	This work
Antarctica, 1995 ($n = 2$)	600	$1.1 \times 1.3^{\pm 1}$	$0.2 \times 1.0^{\pm 1}$	$1.0 \times 1.1^{\pm 1}$	This work
Bavaria, 1998/1999 ($n = 5$)	800–900	$41 \times 1.4^{\pm 1}$	$1.9 \times 2.0^{\pm 1}$	$109 \times 1.5^{\pm 1}$	This work
Bavaria, 1995 ($n = 12$)	800–900	—	$1.4 \times 1.8^{\pm 1}$	$329 \times 2.4^{\pm 1}$	Schnell (1997)
Lower Saxony 1999 ($n = 7$)	600–700	$4.8 \times 1.4^{\pm 1}$	$3.5 \times 1.6^{\pm 1}$	$168 \times 1.5^{\pm 1}$	Ernst et al. (2003)
Moscow, Russia, 1996 ($n = 2$)	—	$4.1 \times 1.2^{\pm 1}$	$0.7 \times 1.5^{\pm 1}$	$49 \times 1.5^{\pm 1}$	Michel et al. (2005a)
Russia, pre-nuclear	—	—	—	0.08 ± 0.02	Szidat et al. (2000)
Zhitomir, Ukraine, 1997 ($n = 12$)	—	$4.6 \times 1.3^{\pm 1}$	$0.4 \times 1.3^{\pm 1}$	$38 \times 1.7^{\pm 1}$	Michel et al. (2005a)

D: deposition density; n: number for samples.

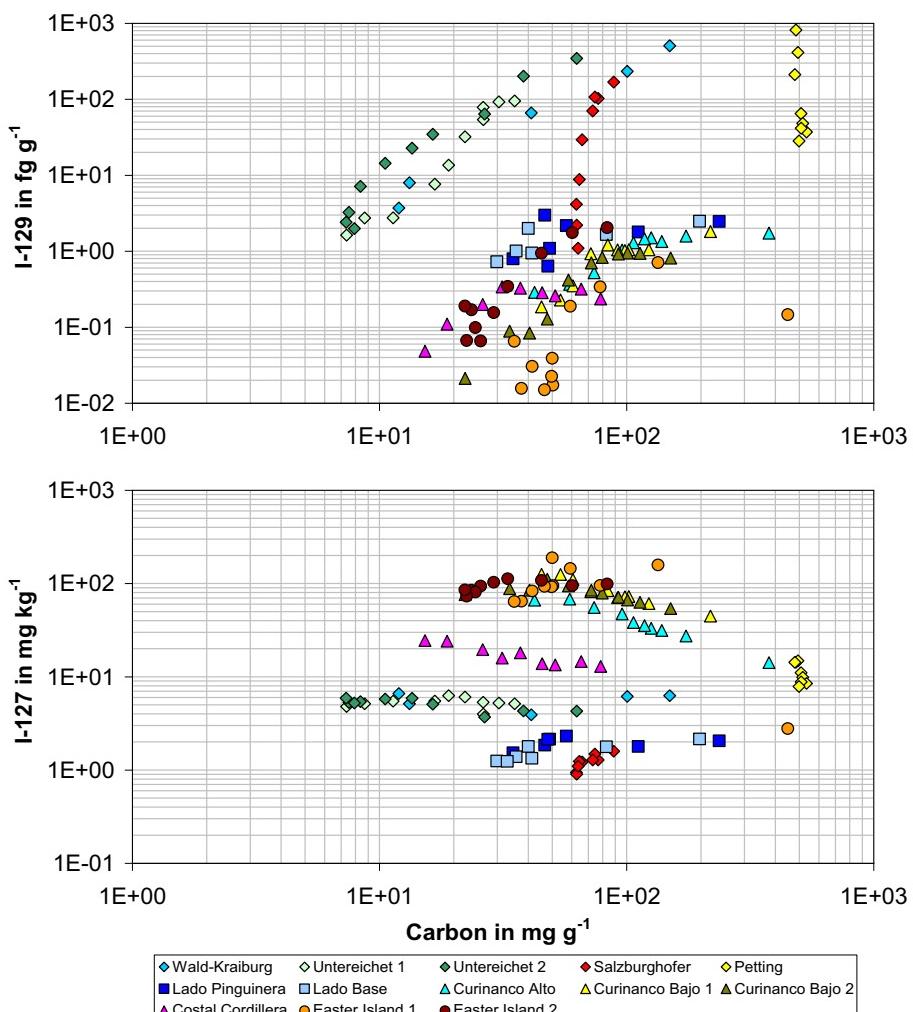
^a Reference date: 26.4.1986.

inventories are just around 1 mBq m^{-2} . Since from the Fiescherhorn ice core it can be firmly concluded that the annual deposition rates in the pre-nuclear age were below $0.01 \text{ mBq m}^{-2} \text{ a}^{-1}$ and since the profiles of the ^{129}I activity concentrations are decreasing with depth and do not reveal an approximately constant shape to be expected in equilibrium, one has to discuss the Chilean data as consequence of man-made ^{129}I originating from two sources: fallout from the atmospheric nuclear weapons explosions and continuous fall-out of ^{129}I from precipitation which itself originates from the modern oceanic missing zone.

For the modern oceanic mixing zone, only an $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of about 10^{-10} can be assumed from the measurements of

Kilius et al. (1994) for the Californian Pacific Coast in 1992/1993, Yiou et al. (1994) for the North Atlantic near Iceland in 1990/1991 and by Michel et al. (2012) for the pacific near Hawaii in 1997 and the Indian Ocean in 2005. There are up to now no measurements from the oceans in the Southern Hemisphere and it is unknown how long back a $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of about 10^{-10} has to be assumed for the global oceanic mixing zone.

One decade of precipitation with an annual rate of 1000 mm with a $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of 10^{-10} and consequently a ^{129}I concentration of $4 \times 10^{-18} \text{ g g}^{-1}$ would result in an annual deposition rate of 0.26 mBq m^{-2} . This adds considerable uncertainty to an interpretation of the observed Chilean ^{129}I inventories of about

**Fig. 5.** The association of ^{129}I (top) and of ^{127}I (bottom) with carbon in the soil.

1 mBq m⁻² as the result of solely the fall-out of the atmospheric nuclear weapons explosions. Considering, moreover, that the integrated deposition at the Fiescherhorn on the Northern Hemisphere up to 1965 just yielded 0.6 mBq m⁻² (Wagner et al., 1996; Reithmeier et al., 2006), causes further doubt that the Southern Hemisphere had ¹²⁹I bomb fall-out of about 1 mBq m⁻².

Assuming the actual mean annual precipitation rates at Valdivia of 2700 mm and at the Easter Island of 1100 mm, about 20 years of precipitation with ¹²⁹I/¹²⁷I isotopic ratios of 10⁻¹⁰ would be sufficient to explain the observed inventories. The inventory observed in Antarctica, where we have to account for an annual precipitation – mostly as snow – of 800 mm, cannot be explained in this way: there remains an ¹²⁹I deficit of about 0.6 mBq m⁻² which could serve as an upper estimate of the inventory of the bomb fall-out in Antarctica. In our opinion, this value equals just by chance the “bomb integral” in the Fiescherhorn ice core (Wagner et al., 1996; Reithmeier et al., 2006), since the bomb fall-out in the Southern Hemisphere should be lower than in the northern one as it is revealed by the data for ¹³⁷Cs.

A large influence of Chernobyl fall-out was observed in southern Germany with a ¹³⁷Cs inventory being higher by a factor of about 7 in Southern Germany than in Lower Saxony, Moscow and Zhitomir. ¹³⁷Cs in Bavaria, and in particular in the sampling region, is dominated by the Chernobyl fall-out compared to about 5 kBq m⁻²

(reference date 1986) fall-out from atmospheric nuclear weapons explosions. In the pre-alpine areas of Southern Germany the average ¹³⁷Cs deposition amounted to 32 kBq m⁻² (SSK, 1987, 1996), well in agreement with the results from this work (Table 2). The weapons fall-out inventories are seen in our work in the data for Lower Saxony, Moscow/Russia, and Zhitomir/Ukraine, which all got just minor fall-out from the Chernobyl accident.

According to the global ¹³⁷Cs fall-out distribution predicted by UNSCEAR (1982) the ¹³⁷Cs deposition densities in Chilean soils were expected to be much lower than those found in areas near the latitude of 40°S (Schuller et al., 2002). The ¹³⁷Cs deposition densities resulted from measurements carried out between latitudes of 27°S (Easter Island) and 63°S (Antarctic Peninsula region) on the Chilean territory did not indicate any dependency on the geographical position (Schuller et al., 1997, 2004). However, they exhibited a significant dependency on the mean annual rainfall rate.

In Chile, the ¹³⁷Cs inventories (reference date 1986) from this work were between 0.64 kBq m⁻² and 3.72 kBq m⁻² with a geometric mean of (1.7 × 2.0^{±1}) kBq m⁻². This is just a factor of 3 lower than the weapon's fall-out in Germany. The data are surely not affected by fall-out from the Chernobyl accident and can completely be attributed to the atmospheric nuclear weapons explosions.

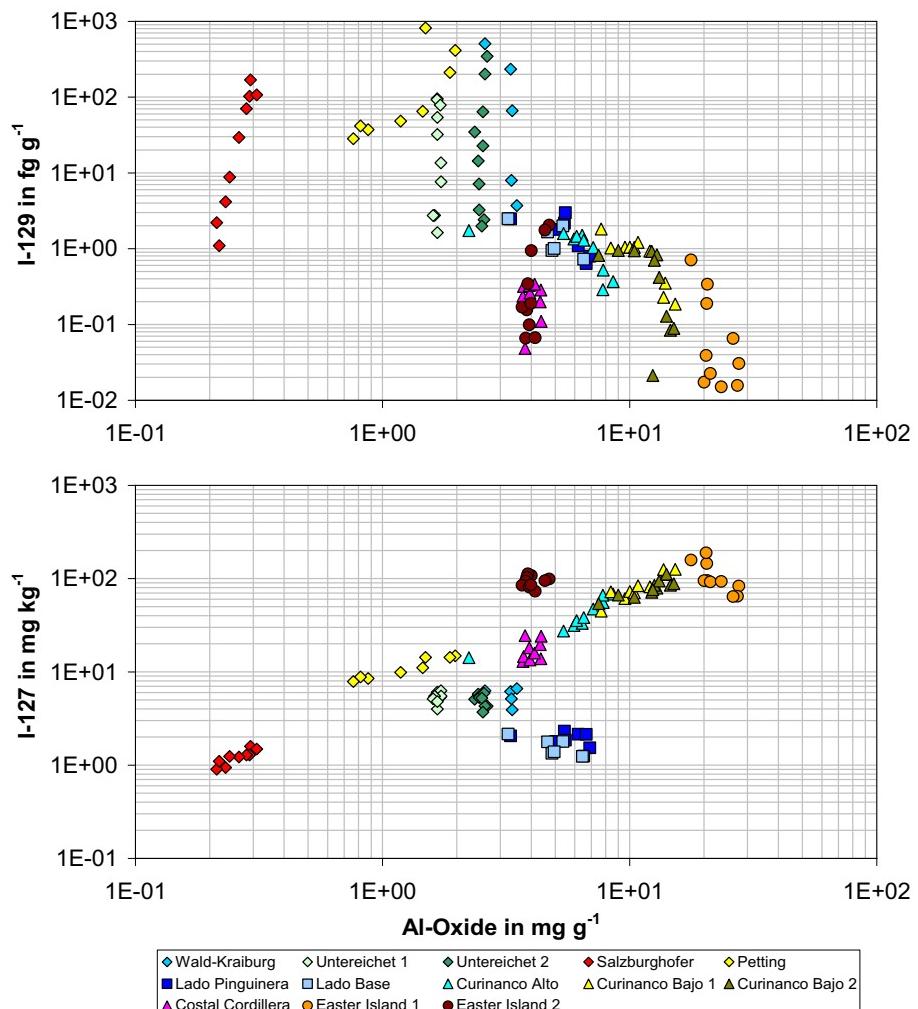


Fig. 6. The association of ¹²⁹I (top) and of ¹²⁷I (bottom) with aluminium oxide in the soil.

3.4. Association of the iodine isotopes with soil properties

The associations of the ^{127}I and ^{129}I concentrations with the soil properties demonstrate the complexity of iodine adsorption and migration in the soils. There are completely different patterns for ^{127}I and ^{129}I . Despite of different soil types one observes the following features: The ^{129}I activity concentrations show a positive association with the C_{org} -concentration (Fig. 5) and show the same association with nitrogen and sulphur (not shown), which are also constituents with organics in the individual soil profiles. But, such an association is not seen for the ^{127}I concentration.

In spite of the same physical and chemical behaviour of the isotopes, ^{127}I and ^{129}I , they undergo evidently different sorption processes in the soils. Surely, this is not an isotope effect but a consequence of the migration processes on differing time scales.

To explain these, we must take into account the different histories of the two iodine isotopes in the soils. It is meaningful to distinguish "old" and "modern" iodine in the soils. Old iodine was brought into the soils over long times-scales and likely had a $^{129}\text{I}/^{127}\text{I}$ isotopic ratio of $\sim 10^{-12}$. Modern iodine was deposited after 1945 and had $^{129}\text{I}/^{127}\text{I}$ isotopic ratios of 10^{-10} and higher.

As pointed out by Ernst et al. (2003) the immobilisation, i.e. the sorption of ^{127}I and ^{129}I in the soils from Lower Saxony could only be understood as a time-dependent kinetic process involving unspecific and specific adsorption processes strongly depending on the hydrological situation.

Immobilisation of newly precipitated iodine is only possible in the soil if exchange between already bound old iodine in the soil and the mobile iodine in the soil water is possible on the time scale of the fall-out. The likelihood of this exchange is determined by the absolute $^{129}\text{I}/^{127}\text{I}$ ratio of the free iodine taking into account possible co-adsorbing species and the reversibility of the adsorption. The reversibility of the adsorption is given by the thermodynamic stability of the adsorbate, i.e. of the formation of the complex between the adsorbing agent and the adsorptive. Adsorbates which are more stable in the thermodynamic sense form preferentially and exhibit the smallest reversibility.

Since iodine is biophilic it will be adsorbed to the organic matter which is an adsorbate of low thermodynamic stability and which over long time scales will be mineralised. If over long time scales the organics in the soils would be stable, one would expect a positive association between ^{127}I and the organics. This is not the case.

Because of the longer interaction times and the higher concentration of ^{127}I compared to ^{129}I , ^{127}I preferentially occupies the thermodynamically favourable sorption places. Without newly generated sorption places, which can lead to an irreversible ^{129}I adsorption, virtually no irreversible adsorption and immobilisation of modern iodine can take place.

But, there are positive associations of the ^{127}I concentrations with the concentrations of aluminium oxides (Fig. 6) and iron oxides (not shown). There is a dramatic variability of about one order of magnitude, each in the aluminium as well as in iron oxide concentrations. In the individual profiles both oxides are relatively constant. Some variation is seen both for aluminium and iron oxides only in the upland moor profile Petting. For ^{129}I no such correlations between the concentrations and the metal oxide concentrations are observed.

The ^{127}I concentration in soils must be assumed to reveal the result of an equilibrium situation of constant influx by precipitation, exchange between mobile iodine in the liquid and sorption desorption, run-off with surface water and migration inside and through the soil into deeper groundwater over long time scales. Therefore, the concentrations of stable iodine reflect the thermodynamically stable adsorbates, here aluminium oxides and iron oxides, with which they can undergo stable chemical adsorption.

4. Conclusions

We report here inventories of the ^{137}Cs and ^{129}I in the environment, in Bavaria in South Germany, Central Chile, Chilean Antarctica and Easter Island. The ^{137}Cs contaminations of the areas from Southern Germany caused by the global fall-out after the nuclear weapons tests are about 4 kBq m^{-2} (BstMLU, 1988) and are dominated by the Chernobyl fall-out. The mean deposition density is $(41 \times 1.4^{\pm 1}) \text{ kBq m}^{-2}$ in these areas. There was only an influence from the global fall-out from nuclear weapons testing, but no fall-out from the Chernobyl accident at the Chile and Easter Island with a ^{137}Cs inventory of $(1.7 \times 2.0^{\pm 1}) \text{ kBq m}^{-2}$. The relatively high ^{137}Cs inventories at some areas in Chile can be attributed to the high annual rainfall at these places as compared to others.

On other side, we observed a large and continuous influence of on-going releases of ^{129}I from the European reprocessing plants La Hague in France and Sellafield on northern Germany with total inventories of $(168 \times 1.5^{\pm 1}) \text{ kBq m}^{-2}$ (Ernst et al., 2003), and on Southern Germany with $(109 \times 1.5^{\pm 1}) \text{ kBq m}^{-2}$ in this work. In Eastern Europe, Michel et al. (2005b) obtained for the average of Moscow and Zhitomir an inventory of $(40 \times 1.6^{\pm 1}) \text{ kBq m}^{-2}$. Both, the values for Germany and Eastern Europe are much larger than the corresponding ones for the soil samples from Chile and Easter Island which showed total inventories of only $(1 \times 2^{\pm 1}) \text{ kBq m}^{-2}$. The results for the soils from Chile can be regarded as an estimate of the ^{129}I fall-out from the atmospheric nuclear weapons explosions in the Southern Hemisphere.

The migration behaviour of ^{127}I and ^{129}I remains an unresolved issue, being influenced by many environmental factors. An important clue may be that the ^{127}I , which was mainly input into the soils over long time scales, behaves differently than the modern ^{129}I . The association between soil properties and ^{127}I and ^{129}I point to a time-dependent sorption process starting with weak sorption to organic matter followed by a stronger sorption to mineralised soil components.

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